MAC-INNES

A Comparative Study of the Dissociation Relations of Caesium Nitrate, Potassium Chloride, and Lithium Chloride in Aqueous Solution at Zero Degrees

Chemistry

PH. D.

1911

UNIV. OF
ILLINOIS
LIBRARY

UNIVERSITY OF ILLINOIS
LIBRARY

Class 1911
Book M11
Volume

Monastery Hill
Chicago

Digitized by the Internet Archive
in 2016

https://archive.org/details/comparativestudy00maci

A Comparative Study of the Dissociation Relations of Caesium Nitrate, Potassium Chloride, and Lithium Chloride in Aqueous Solution at Zero Degrees

938
12
M13

BY

DUNCAN ARTHUR MAC-INNES
B. S. University of Utah, 1907
M. S. University of Illinois, 1909

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1911

1911
M11

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 13, 1911

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Duncan Arthur MacInnes

ENTITLED A Comparative Study of the Dissociation Relations of Caesium Nitrate, Potassium Chloride, and Lithium Chloride in Aqueous Solution at Zero Degrees.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy in Chemistry

E. W. Washburn
In Charge of Major Work

Wm A. Noyes.
Head of Department

Recommendation concurred in:

C. W. Balke.
A. P. Carman
R A Curtiss

Committee
on
Final Examination

197275

The following work was undertaken in the Chemical Laboratory of the University of Illinois at the suggestion of Professor E. W. Washburn. It was begun in the fall of 1908 and continued until the spring of 1911.

I wish to take this opportunity to thank Professor Washburn for the inspiration and help he has given me during the course of this investigation.

The Rare Book & Manuscripts Library UIUC

A COMPARATIVE STUDY OF THE DISSOCIATION RELATIONS OF CAESIUM NITRATE, POTASSIUM CHLORIDE, AND LITHIUM CHLORIDE IN AQUEOUS SOLUTION AT ZERO DEGREES

Introduction:

The following investigation was undertaken for the purpose of extending our knowledge of aqueous solutions of strong electrolytes in moderately concentrated solutions. Caesium nitrate was chosen for study as it is of the simplest possible type and from the fact that it is probably hydrated little, if at all, in solution. For the purpose of comparison lithium chloride was chosen, being most hydrated of salts of this type, and potassium chloride was included, as, in this respect, it occupies an intermediate position between the first two salts.

The experimental work consisted of freezing point determinations, and conductance, density and viscosity measurements at 0°.

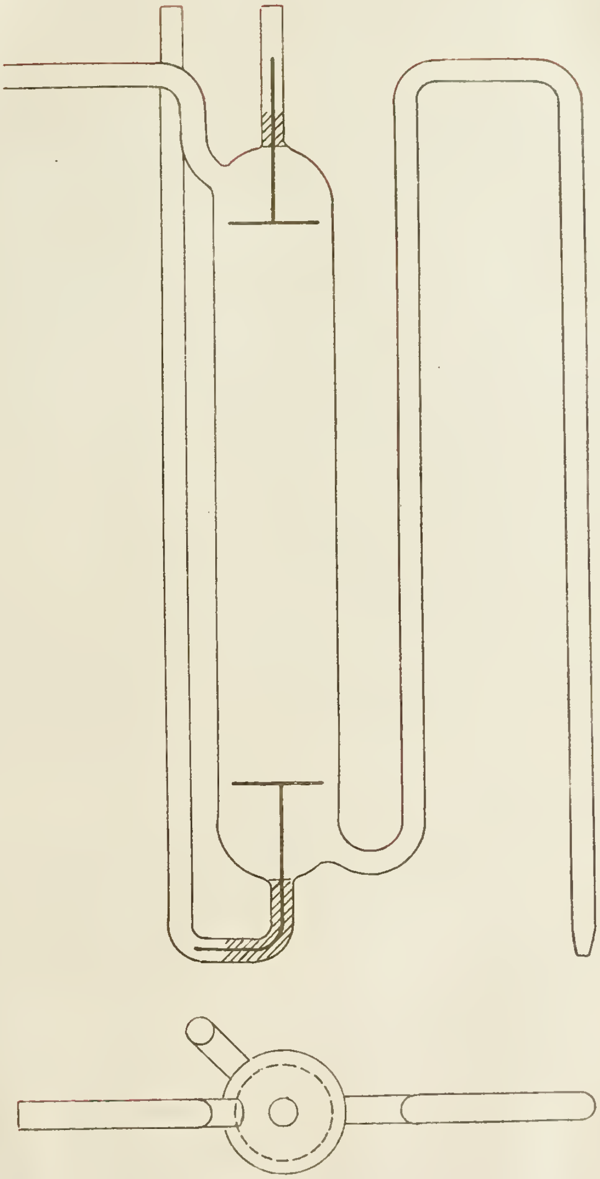


Fig. 1.

1- Description of Apparatus and Methods

(a) The Conductance Measurements. A Kohlrausch slide wire bridge was used in the conductance measurements. The wire had a length of about three meters, the smallest scale division being 3 mm. It was calibrated against standard resistance boxes by a method described by Kohlrausch and Holborn[1]. This calibration was repeated from time to time whenever it became necessary to clean the wire. The resistance box used was calibrated and found to be correct within the limits of error of the work.

The alternating current was furnished by a small induction coil, provided with an adjustable resistance in series with its primary. As recommended by Kohlrausch[2], a small adjustable condenser was placed in parallel with the resistance box. With this arrangement it was possible to obtain complete silence in the telephone receiver at the null point, for all except the most dilute solutions, provided the conductance capacity of the cell was adapted to the solution which it contained. Under these conditions check readings could readily be made to one tenth of the smallest scale division or to 1 part in 5000.

The cells used were of the pipette type shown in figure 1, and were made of Jena Geräte glass. The internal diameter of the cells was about 15 mm., and the electrodes were one centimeter in diameter. Three cells were employed with electrodes 75 mm., 15 mm. and 2 mm. apart, respectively. The first cell gave perfect minima for salt solutions ranging in concentration between N/1 and N/10, the second for those between N/10 and .005 N. The third was used for the most dilute solutions. The electrodes were coated with platinum black in the usual manner. The con-

---

[1] Kohlrausch and Holborn, Leitvermogen der Electrolyte, pg. 47.

[2] Ibid.- pg. 59.

ductance capacities of the first two cells were determined by measurments with normal and tenth normal solutions of potassium chloride as directed by Kohlraush and Holborn[3] and the values used for the specific conductances of these solutions at 0° were 0.06541 and 0.007150 mhos, respectively. The constants found by measurments with solutions prepared at two different times are as follows:-

Date-	Oct. 19, 1910.		Jan. 1,1911.	
Solution-	N/1	N/10	N/1	N/10
Cell 1.	3.423	3.425	3.423	3.424
Cell 2.	- - -	0.6222	- - -	0.6222

The capacity of the smallest cell (0.01592) was determined in terms of that of the second cell by measurments with the same dilute solution in both. The conductance of the water was determined in a cell of the usual **Arrhenius** type with unplatinized electrodes 3 cm. in diameter and about 2 mm. apart. The measurments of the conductance of the water used gave results agreeing within about 2 percent, which was as accurate as was necessary. All conductances were made at 0°, a large Dewar tube filled with a mixture of water and finely chopped ice being used as a constant temperature bath. This mixture was kept in constant motion by an electrically driven up and down stirrer.

---

[3] Leitvermögen der Electrolyte, pg. 76.

(b) The Specific Gravity Measurments. The pycnometer used was of the Ostwald-Sprengel type, with a glass cap ground on the end of one capillary tube and a small bulb blown in the upper part of the other to allow for expansion of the liquid contained. This was necessary as the pycnometer was filled at 0° and weighed at room temperature. A second pycnometer was used as a counterpoise when weighing. The capacity of the pycnometers was about 25cc. All specific gravities are at 0° referred to water at 4° C.

(c) The Freezing Point Measurments. The freezing point of an aqueous solution is the temperature at which it is in equilibrium with ice. To obtain this temperature accurately it is necessary to have the two phases in intimate contact. The Beckmann method is unsuitable for accurate work as one can never be certain that equilibrium has been reached owing to the small amount of ice separating out. Corrections must also be applied for "convergence temperature" and concentration changes due to the separation of ice. It was therefore decided to use the "equilibrium" method,[4] in which the temperature of a mixture of the solution with an excess of finely broken ice is determined, and a portion of the solution is then drawn off and analysed.

The freezing point vessel was a silvered Dewar tube of 150 cc. capacity. The Dewar tube was surrounded by a bath composed of a mixture of fine ice and water. Through openings in the cover of the tube were inserted a Beckmann thermometer, a stirrer, and a tube T of small bore which was used for withdrawing solution. In order to prevent the removal of ice the tube was drawn out to a capillary at its lower end. An electrically operated tapper was used to give a

---

4- For references to previous work with this method see Ostwald-Luther, "Physico-chemischen Messungen", Ed. 3, pg. 281.

uniform agitation to the mercury thread of the thermometer.

Pure ice was prepared by placing test tubes containing conductivity water in a freezing mixture. The ice collected on the walls of the tubes, and the central portion , containing any impurities present, was poured off. The ice was then broken into small lumps in a mortar that had been previously chilled by filling it with fine ice. These lumps were placed in the Dewar tube until it was about three fourths filled, and the solution, having about the concentration desired, was cooled to its freezing point and poured over the ice. The Beckmann thermometer, stirrer, and the tube T were then inserted and the vessel covered. With slow stirring the thermometer soon gave constant readings. As the temperature of the surroundings never differed by more than 1.5° from that of the mixture in the Dewar tube, the ice melted very slowly, and a solution of given concentration could be kept in equilibrium with ice for a considerable time, as was shown by the fact that the thermometer gave constant readings for as long as three quarters of an hour.

After reading the thermometer, the pipette conductivity cell (Fig. 1.) was connected to the tube T by means of a rubber tube and a small portion of the solution withdrawn and rejected. Another sample, which filled the conductivity cell, was immediately withdrawn. To prevent the warmed solution in the upper part of the tube T from falling back when the pipette cell was detached, the rubber connection was closed by means of a pinch cock. After this the thermometer was again read, but in no case was the reading different from the first. The solution in the conductivity cell was next placed in an ice bath in a large Dewar tube. The bath was stirred constantly and as soon as the contents of the cell had

assumed the temperature of the bath its conductance was measured. The concentration of the solution could then be determined by interpolating from the conductance measurments on solutions of known concentration.

Each time the thermometer was used its zero point was determined with pure ice and water. The readings of the thermometer were always made with a rising meniscus, with the tapper temporarily stopped, and at a definite room temperature, the last precaution making stem exposure corrections unnecessary.

The Beckmann thermometer was carefully calibrated for irregularities of bore by the usual method of a moving mercury thread. The value of a degree in terms of the standard hydrogen thermometer was found by comparison with a Beckmann thermometer standardized by the U.S. Bureau of Standards. For two weeks before the beginning of the investigation, and when not in use until its completion, the thermometer was kept in an ice bath in order to protect it from large changes of temperature.

(d) The Viscosity Measurments. The relative viscosities of the salt solutions were measured at0° in viscosimeters of the Ostwald type. As the entrance of warm air into the apparatus during a determination was found to affect the results, the upper ends of the viscosimeter tubes were connected by a device similar to that used by Archibald, McIntosh and Steele,[5] and the whole apparatus was immersed in a constantly stirred mixture of fine ice and water. With this arrangement the liquid flowing from the upper bulb of the viscosimeter was replaced by cold air from the opposite tube. The capillary tubes of the viscosimeters were 12 cm. long and about 0.02 bore. The upper and lower bulbs, the centers of which were at a difference of level of 16 cm., had capacities of 7 and 40 cc., respectively. In order to have the viscosimeters in the same position during all the measurments, a special holder was constructed.

Before each set of measurments the viscosimeters were cleaned by filling them with concentrated nitric acid containing a few drops of alcohol, and allowing them to remain over night. They were then rinsed several times with conductivity water and with the solution whose viscosity was to be measured, and allowed to drain. A definite quantity of the solution was then introduced from a pipette.

Great care was taken to have the solutions and the water free from dust particles as they are liable to affect the results by lodging in the capillary. When necessary, the solutions were filtered through specially cleaned hardened filter paper.

The potassium chloride solutions were made up from weighed quantities of the fused salt and water. The concentrations of the

---

5- Z.Physik. Chem.55. 129. (1907), also Ostwald-Luther, "Physico-chemische Messungen" Ed.3, pg. 233.

lithium chloride solutions were determined by measurments of their conductances and interpolating from the conductance-concentration table for that salt given elsewhere in this paper. In making up the solutions, and for the determination of the water value of the viscosimeters. the best conductivity water was used.

The time of flow was measured with a stop watch which could be read to 1/5 second. The period for water was about 300 seconds and check determinations agreed within 2/5 second or to 0.13 percent. Duplicate measurments of the time of flow of the solutions checked within 1/5 second or to 0.07 percent.

The relative viscosity η/η_0 was calculated from the formula- $\frac{\eta}{\eta_0} = \frac{D\, t_s}{t_w}$, where D and t_s are the density ($0^{\circ}/0^{\circ}$) and time of flow, respectively, for the solution, and t_w the time of flow of the water.

The densities were interpolated from tables 3 and 4 of this paper.

2- Preparation and Analysis of Solutions.

As there are no quick and accurate analytical methods for the determination of caesium or of nitrates the solutions of this salt whose freezing points had been found were analyzed by measuring their conductances and interpolating from a series of conductances measurments on salt solutions of known concentration (Table 3). This same procedure was adopted in the case of lithium chloride solutions on account of its rapidity and convenience.

Caesium nitrate solutions of definite concentration were prepared by weighing the fused salt into glass stoppered Jena flasks, adding conductivity water and again weighing. From these solutions a series of more dilute solutions were prepared by weight. Solutions made directly from the salt are marked by an asterisk in Table 3 . Solution No. 6 was prepared from a different sample of caesium nitrate as a check. The caesium nitrate for this solution was prepared from Kahlbaum's best caesium chloride by four evaporations with pure concentrated nitric acid and the repeated crystallization of the product from conductivity water at 0°, using centrifugal drainage.

The more dilute solutions, .03N and less, were found to be readily contaminated by contact with the air and by long standing in the flasks. To overcome these sources of error, the flasks, previously weighed, were filled with fresh, hot conductivity water directly from the still, and allowed to stand over night. The following day they were rinsed thoroughly and then weighed together with the required quantity of conductivity water. A portion of a freshly prepared solution of known concentration was then added and the flask and contents reweighed. By this method the flasks were not dried before the solution was made up and the impurities in the adhering water were not retained in the flask. The quantities of

water and solution were adjusted so that but a small air space remained below the stopper. As there was a possibility that adsorbtion of salt by the platinum black of the electrodes might contaminate dilute solutions, even when the cell was cleaned between each two determinations, the conductance of the most dilute solution was measured first and the others in order of their strengths. Frequent measurments were made of the conductance of the water used.

The series of lithium chloride solutions of known concentration was made by the dilution, as described above, of two solutions, Nos. 1 and 6. These were analysed as follows:- weighed quantities of the solution were treated with an excess of silver nitrate solution. The precipitates were collected in Gooch crucibles and washed with $\frac{1}{1000}$ normal silver nitrate solution and with a small volume of a very dilute nitric acid solution, and finally dried in an air bath at 150°. The results from the two solutions are as follows:-

Solution.	Weight of sample.	Wt. Ag Cl.	Conc. Mols per 1000gr Solution
1	25.184	2.1754	0.6026
"	25.115	2.1714	0.6032
6	99.608	.4755	0.03331
"	99.555	.4756	0.03333

3-Purification of Materials.

Caesium Nitrate:- The method of purification used was that described by J. Lawrence Smith.[6] Kahlbaum's purest caesium carbonate was dissolved in the smallest amount of nitric acid. Solid iodine and hydrochloric acid were then added in the proportions necessary to form $CsCl_2I$, and the mixture was heated. The caesium chlor-iodide separated as orange colored crystals upon cooling. The crystals were filtered from the mother liquor and dried as far as possible by suction. The crystallization was repeated three times from hot hydrochloric acid (1 to 1), drying the crystals between each two operations. The final product was heated over a flame in a casserole to remove the iodine and the excess chlorine and the resulting caesium chloride was converted into nitrate by four evaporations with pure nitric acid. (The pure nitric acid was obtained by distilling ordinary pure acid and reserving the second third of the distillate.) The caesium nitrate thus obtained was crystallized four times from conductivity water and the final product was dried in an air bath.

Lithium Chloride:- Kahlbaum's best lithium chloride was purified by a method suggested by Kahlenburg and Krauskopf.[7] A saturated solution of the dried salt in carefully dried pyridene was made at 90°, and filtered hot through a hardened filter paper. The solution was allowed to cool and the salt which separated was freed from the mother liquor by filtration with suction. The salt was then placed in a distilling flask and the remaining pyridene driven off. The product thus obtained was evaporated to dryness twice with pure concentrated hydrochloric acid, and finally heated for several hours in an air bath at 150°.

Potassium Chloride:- Kahlbaum's purest potassium chloride was recrystallized four times from conductivity water and dried between filter

---

6-Am. Jour. Sci., 11, 16, pg. 373.
7-Jour. Am. Chem. Soc. 30, 1104, (1908.)

paper.

Water:- All the water used in this investigation was conductivity water obtained from the special still[8] in this laboratory. It was collected hot and kept in bottles made of Whitall and Tatum's "Non-sol" glass. The conductance of the water at 0^0 averaged 0.4×10^{-6} mhos.

---

[8] The form of the still is described by Noyes and Coolidge, Proc. Am. Acad., 39, 190, (1903), and Carnegie Inst. Pub., No.63, pg. 39, (1907).

4-The Freezing Point Data.

The results obtained in the freezing point measurments on the caesoum nitrate solutions are shown in the following table, in which n' represents mols of $CsNO_3$ per 1000 grams of water.

Table *I* .

	1	2	3	4	5	6	7	8	9	10	11
n'	0.0185	0.0525	0.1296	0.1595	0.1855	0.2169	0.2729	0.2816	.3212	.4148	.4370
Δt	0.067	0.174	0.418	0.507	0.582	0.666	0.824	0.852	0.949	1.203	1.254

The strongest solution studied (n'=0.4370) was in equilibrium with both ice and solid $CsNO_3$, so that the eutectic or cryohydric point for this salt is -1.254°.

All of the data shown in the above table were treated by the method of least squares and the following equation was obtained:-

$$\Delta t = (3.426\, n' - 1.862\, n'^2 + 1.373\, n'^3) \pm 0.0016^\circ \qquad (1.)$$

The probable error, 0.0016°, is that given by the relation $P.E. = 0.675\sqrt{\frac{\Sigma D^2}{n-1}}$, where ΣD^2 is the sum of the squares of the deviations of the observed values from those calculated by means of equation 1.

. The largest deviation was 0.005° and the others were all less than 0.003°. It seems improbable, therefore, that the freezing point lowerings calculated from equation 1. will be in error by more than 0.002° as a result of chance fluctuations of the individual observations.

In table 2 are shown the results of freezing point measurments on lithium chloride solutions. As in the previous table, the concentrations, n', are expresed in mols of the salt per 1000 grams of water. The measurments on solutions No's 10 and 11 only were made in the present investigation. The other values given in this table are those obtained by Jahn [9], by a method similar to that described in this paper.

---

[9] Z. physik. chem., 40, 185 (1902).

Table 2.

	1	2	3	4	5	6	7	8	9	10	11
n'	0.02503	0.03771	0.05053	0.07462	0.09732	(0.1508)	0.2038	0.2544	(0.2938)	0.3378	0.4549
Δt	0.0909	0.1352	0.1794	0.2648	0.3431	(0.5232)	0.7093	0.8879	(1.0377)	1.177	1.602

These results are expressed by the equation:-

$$\Delta t = (3.594\, n' - 0.7916 n'^{2} + 1.3910\, n'^{3}) \pm 0.001^{\circ} \qquad (2)$$

also obtained by the application of the method of least squares to the results. The values in parenthesis, No's 6 and 9 were not used in deriving equation 2 as they lie considerably off the smooth curve obtained by plotting the other results.

5-The Conductance and Density Data.

Caesium Nitrate and Lithium Chloride. The concentrations, n', of the solutions, expressed in mols of the salt per 1000 grams of water are given in column 1 of tables 3+4 and the corresponding densities and specific conductances in columns 2 and 3. The densities are referred to water at 4°. The specific conductance of the water used in preparing the solutions has been subtracted from each specific conductance given in the tables. The cells used in determining the conductances are shown in column 4. (See page 2.)

6-The Viscosity Data.

Lithium Chloride and Potassium Chloride. Table 5 gives the results of the viscosity measurements with solutions of these two salts. In column 1 are given the concentrations in mols per 1000 grams of water and in column 3 the relative viscosities of the solutions, calculated as described in Sec. 1. The density values for lithium chloride were interpolated from the data given in table 4. Those for potassium chloride were interpolated from the very accurate results of Freund.10)

10-Z. physik. chem. 66, 580(1909)

Table 4

Conductivity and Density Data

Lithium Chloride Solutions at 0.000°.

Nº	n'	$D\,{}^{0°}/_{4°}$	Corrected Specific Conductance × 10^6.	Cell Nº
1	0.6187	1.0151	26230.	1
2	.3659	1.0093	16650.	1
3	.3561	1.0088	16260.	1
4	.2144	1.0054	10270.	1
5	.07702	1.0021	3988.	2
6	.04120	1.0009	2210.	2
7	.03337	1.0007	1801.	2
8	.01646		917.2	2
9	.008322		474.2	3
10	.002027		118.8	3
11	.001039		61.33	3
12	.000578		30.66	3

Specific Conductance of the Water = $0.49.10^{-6}$

Conductivity and Density Data Continued

Table 3

Caesium nitrate solutions at 0.000°

Nº	n'	$D^{0^\circ}_{4^\circ}$	Corrected Specific Conductance $\times 10^6$	Cell Nº
1	0.5389 *	1.07705	30900.	1
2	.4482	1.0630	26350.	1
3	.4427 *	1.0623	26110.	1
4	.3346	1.0475	20420.	1
5	.3078	1.0425	18980.	1
6	.2498 *		15740.	1
7	.2383 *		15060.	1
8	.1612	1.0222	10700.	1
9	.1529	1.0215	10170.	1
10	.1059 *	1.0145	7262.	2
11	.09314 *	1.0074	6461.	2
12	.05962	1.0056	4315.	2
13	.04666	1.00206	3397.	2
14	.01730	1.0015	1336.	2
15	.008877		702.2	2
16	.003940		318.0	3
17	.001737		141.3	3
18	.0004414		36.44	3
19	.0002115		17.61	3

Specific Conductance of the Water = $0.44.10^{-6}$

Table 5 and 5a

Viscosity Data at 0.000°

No.	Conc. Mols per 1000g. water.	Density $D\frac{0°}{0°}$	Relative Viscosity η/η_0
		Potassium Chloride	
1	0.5160	1.0249	0.9569
2	.4063	1.0197	.9654
3	.3015	1.0146	.9752
4	.2118	1.0104	.9864
5	.1042	1.0051	.9944
		Lithium Chloride	
1	0.6036	1.0151	1.0813
2	.3508	1.0088	1.0481
3	.3247	1.0082	1.0434
4	.2540	1.0066	1.0337
5	.1077	1.0029	1.0125

7- Summary of Data at Round Concentrations.

The first seven columns of tables 6, 7, and 8 contain the values of the freezing point lowerings, densities, relative viscosities, specific conductances and equivalent conductances at round concentrations for the three salts investigated. In the first column of each table are given the concentrations of the solutions expressed in mols per 1000 grams of water.

The second column contains the corresponding freezing point lowerings. Those for caesium nitrate and lithium chloride were computed from the empirical equations, No's. 1 and 2, derived in section 4. The value of the freezing point lowering for the concentration, n' = 0.025, was, however, obtained by a graphical interpolation from the observed values. The $CsNO_3$ solution with a concentration, n' = 0.5, to which a freezing point lowering of 1.419° ± 0.005° is assigned, is a supersaturated solution. This value for Δt was obtained from equation (1), but as this involves an extension of the equation beyond the limits for which it was derived a graphical extrapolation was made as a check. For this purpose a plot of equation (1) was made on cross section paper. A flexible rod of celluloid was then made to pass through all the of the points plotted, the highest point being that for the concentration 0.4370 The portion of the rod projecting beyond this was then grasped by one man while a second man sighted along the rod from the opposite end and the first man shifted the position of the upper end until, in the judgement of the second man, it made a smooth curve with the remainder of the rod. The value of Δt for the concentration 0.5000 was then read off. This process was repeated five times with three different men and the following results obtained:- 1.417, 1.420, 1.417, 1.418, 1.418, mean: 1.4178°, which checks the value calculated from equation (1) within 0.002°. Owing

(16a)

Table 6.

SUMMARY OF DATA AT

Caesium Nitrate

Concentration Mols of Salt per 1000 g. H_2O n'	Freezing Point Depression. $\Delta t \pm .002°$	Fr. Pt. Dep. of a Normal Solute $\Delta t_{N.S.}$	Density $D^{0°}_{4°}$ ± 0.01%	Relative Viscosity η/η_0 ± 0.03%	Specific Conductance $\chi \cdot 10^6$ ± 0.1%
0.00000	0.000	0.000	0.9999	1.0000	00000
.02500	.086	.089	1.0030	0.9960	1876
.05000	.168	.175	1.0061	.9905	3634
.07500	.247	.259	1.0104	.9846	5300
.1000	.325	.341	1.0136	.9796	6890
.1500	.477	.503	1.0211	.9700	9991
.2000	.622	.661	1.0278	.9613	12900
.2500	.762	.817	1.0341	.9529	15750
.3000	.897	.972	1.0414	.9446	18610
.3500	1.030	1.122	1.0496	.9368	21230
.4000	1.160	1.271	1.0565	.9291	23870
.4500	1.290	1.418	1.0632	.9212	26440
.5000	(1.419±0.005°)	1.563	1.0710	.9138	28950

ROUND CONCENTRATIONS

Solutions at 0°

Equivalent Condutance $\Lambda \pm 0.1\%$	$\frac{\Lambda}{\Lambda_0} \pm 0.16\%$	$\frac{\Lambda\eta}{\Lambda\eta_0} \pm 0.16\%$	$\gamma = \left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^{0.826}$ $\pm 0.13\%$	$N = \frac{(1+\gamma)n'}{55.53+(1+\gamma)n'}$
(84.0±0.1)	1.0000	1.0000	1.0000	0.0000
75.19	0.8948	0.8912	0.9092	0.0859±0.0001
72.94	.8680	.8597	.8826	.1792±0.0001
70.96	.8445	.8315	.8586	.2504±0.0001
69.32	.8249	.8080	.8385	.3300±0.0002
67.14	.7990	.7750	.8101	.4866±0.0003
65.18	.7757	.7456	.7847	.6387±0.0004
63.89	.7603	.7245	.7663	.7890±0.0004
63.04	.7502	.7087	.7525	.9380±0.0005
61.73	.7346	.6882	.7344	1.0814±0.0006
60.88	.7245	.6731	.7211	1.2247±0.0007
60.10	.7152	.6589	.7085	1.3657±0.00073
59.31	.7058	.6449	.6960	1.5042±0.0008

TABLE 6.

Table 7.

SUMMARY OF DATA AT

Lithium Chloride

Concentration Mols per 1000g H_2O n'	Freezing Point Depression Δt ±.001°	Fr. Dep. of a Normal Solute $\Delta t_{N.S.}$	Density $D\,0°/4°$ ±.01%	Relative Viscosity η/η_0 ±.05%	Specific Conductance $\times 10^6$ ±0.1%
0	0.000	0.0000	0.9999	1.000	0000
0.025	.089	.089	1.0005	1.0028	1363
.050	.178	.176	1.0012	1.0056	2646
.075	.266	.261	1.0020	1.0084	3900
.10	.353	.344	1.0025	1.0116	5038
.15	.526	.511	1.0038	1.0183	7325
.20	.698	.678	1.0050	1.0256	9612
.25	.871	.844	1.0062	1.0330	11770
.30	1.045	1.006	1.0074	1.0404	13890
.35	1.221	1.170	1.0086	1.0475	16000
.40	1.399	1.329	1.0098	1.0544	17940
.45	1.584	1.488	1.0110	1.0612	19840
.50	1.773	1.647	1.0122	1.0679	21730

ROUND CONCENTRATIONS (CONTINUED)

Solutions at 0.000°

Equivalent Conductance $\Lambda \pm 0.1\%$	$\frac{\Lambda}{\Lambda_0} \pm 0.16\%$	$\frac{\Lambda\eta}{\Lambda_0\eta_0} \pm 0.16\%$	$\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^{.94} = \gamma \pm 0.11\%$	$N' = \frac{(1+\gamma)n'}{55.53 \pm (1+\gamma)n'}$
60.31±0.07	1.000	1.000	1000	0.000
54.54	0.9043	0.9068	0.9122	0.0858±0.0001
52.96	.8781	.8830	.8960	.1706±0.0001
51.90	.8606	.8678	.8752	.2526±0.0002
50.47	.8368	.8465	.8550	.3332±0.0002
48.96	.8118	.8267	.8362	.4936±0.0001
48.23	.7997	.8202	.8300	.6548±0.0004
47.53	.7882	.8142	.8243	.8148±0.0005
46.55	.7718	.8030	.8137	.9704±0.0006
46.00	.7627	.7989	.8097	1.1279±0.0007
45.16	.7488	.7895	.8008	1.2807±0.0008
44.44	.7368	.7818	.7935	1.4329±0.0009
43.85	.7271	.7765	.7884	1.5849±0.001

TABLE 7.

(16c)

Table 8.

SUMMARY OF DATA AT

Potassium Chloride

Concentration Mols per 1000 grams H_2O. n'	Freezing Point Depression Δt	Fr. Pt. Dep. of a Normal Solute	Density $D\frac{0^\circ}{4^\circ}$	Relative Viscosity η/η_0	
0.00	0.000	0.000	0.9999	1.000	0.000
0.25	0.087	0.090	1.0012	0.9986	
.05	.175	.177	1.0025	.9974	
.075	.261	.263	1.0037	.9961	
.10	.345	.356	1.0049	.9946	
.15	.513	.518	1.0074	.9916	
.20	.679	.686	1.0098	.9875	
.25	.844	.852	1.0122	.9819	
.30	1.008	1.016	1.0146	.9753	
.35	1.171	1.179	1.0170	.9700	
.40	1.334	1.343	1.0194	.9658	
.45	1.496	1.503	1.0218	.9620	
.50	1.657	1.663	1.0242	.9582	

Solutions at 0.000°

Equivalent Conductance Λ	$\frac{\Lambda}{\Lambda_0} \pm 1\%$	$\frac{\Lambda \eta}{\Lambda_0 \eta_0} \pm 1\%$	$\left(\frac{\Lambda \eta}{\Lambda_0 \eta_0}\right)^{.905} = \gamma$	$N' = \frac{n'(1+\gamma)}{55.53 + n'(1+\gamma)}$
82 ± 0.8	1.00	1.00	1.00	.0000
75.8	0.924	0.923	0.930	.0868 ± 0.0004
73.9	.901	.898	.908	.1715 ± 0.0008
72.5	.884	.881	.892	.2549 ± 0.0012
71.50	.872	.867	.880	.3373 ± 0.0016
70.20	.856	.849	.863	.501 ± 0.002
69.55	.848	.838	.852	.663 ± 0.003
69.08	.842	.827	.843	.823 ± 0.004
68.62	.837	.816	.832	.980 ± 0.004
68.30	.833	.808	.825	1.137 ± 0.005
67.90	.828	.800	.817	1.294 ± 0.006
67.64	.825	.794	.812	1.447 ± 0.007
67.40	.822	.788	.806	1.600 ± 0.007

TABLE 8.

however to the fact that this is an extrapolated value, it seems best on the whole to assign a larger probable error to it, which is placed at 0.005° in the table.

The values of the freezing point depression for potassium chloride are taken from the critical compilation published by Noyes and Falk[11] and are based chiefly upon the results of Jahn[12].

Column 4 contains the densities obtained by interpolation. The values for lithium chloride and caesium nitrate are based upon the data given in tables 3 and 4, while those for potassium chloride are from the data of Freund[13],

The values for the relative viscosity in column 5 were obtained by graphical interpolation. Those for lithium chloride and potassium chloride are based upon the data given in tables 5 and 5a, and those for caesium nitrate are based upon the very accurate work of T. R. Merton.[14]

The specific conductance data are given in column 6. These values were obtained by linear interpolation from the experimental data recorded in tables 3 and 4.

Column 7 contains the values of the equivalent conductances, Λ. The values for caesium nitrate and lithium chloride were calculated from the corresponding density and specific conductance values by the equation:

$$\Lambda = \frac{\kappa\,(1000 + n'M)}{1000\,n'D} \qquad (3)$$

where $\underline{\kappa}$ = specific conductance and M the molecular weight of the salt. For potassium chloride, the values up to and including n' = 0.1 are inter-

---

[11]- Jour. Am. Chem. Soc., 32, 1011, (1910).
[12]- l.c. No. 9.
[13]- l.c. No. 10.
[14]- Trans. Jour. Chem. Soc., 97, 2460 (1910).

polated from Noyes and Coolidges[15] recalculation of the results of Whetham and of Kahlenburg. In order to obtain those for higher concentrations Kahlenburgs values were increased by 0.05 per cent, and the results so obtained were plotted and the values given in column 7 were found by graphical interpolation.

8-Equivalent Conductance at Infinite Dilution.

The extrapolation to infinite dilution, in the case of the equivalent conductances, was made for each salt by the method of A. A. Noyes. Values of the equivalent resistance $1/\Lambda$ were plotted against values of $(C\Lambda)^{n-1}$, and the value of the exponent adjusted until the points fell as nearly as possible on a straight line, and this line was extended to zero concentration. For caesium nitrate, values of these functions for the concentrations- 0.0002115, 0.0004414, 0.001737 and 0.003940 were employed and were calculated from the specific conductivity data of solutions No's. 16, 17, 18, and 19 of table 3. The value of n which fulfilled the above conditions was 1.50. The positions of the points obtained are shown in figure 2. The infinity value thus obtained (84.0) is estimated to be known with a precision of about one unit in the first decimal place. Its accuracy, however, is much less certain than this owing to the the application of the correction for the conductance of the water. For the most dilute solution measured (Sol. No. 19 of table 3) the specific conductance of the water amounted to 4 per cent of that of the solution.

The water correction was applied in the usual manner by subtracting the specific conductance of the water from that of the solution. Since this method of making the correction is perfectly arbitrary the

---

15- Carnegie Inst. Pub. No. 63, pg. 47.

Fig 2.

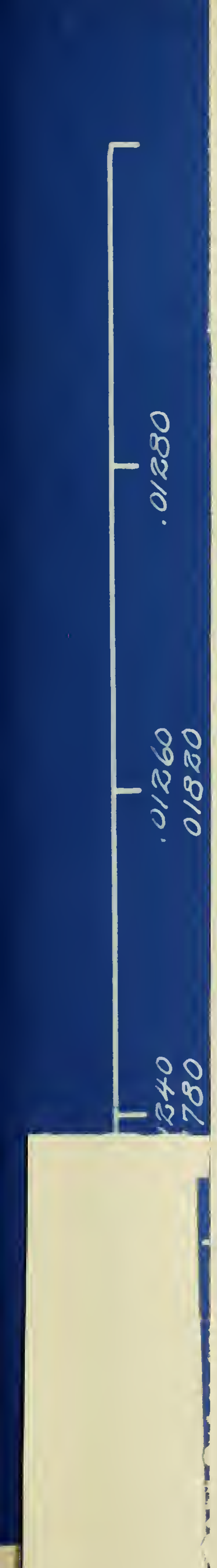
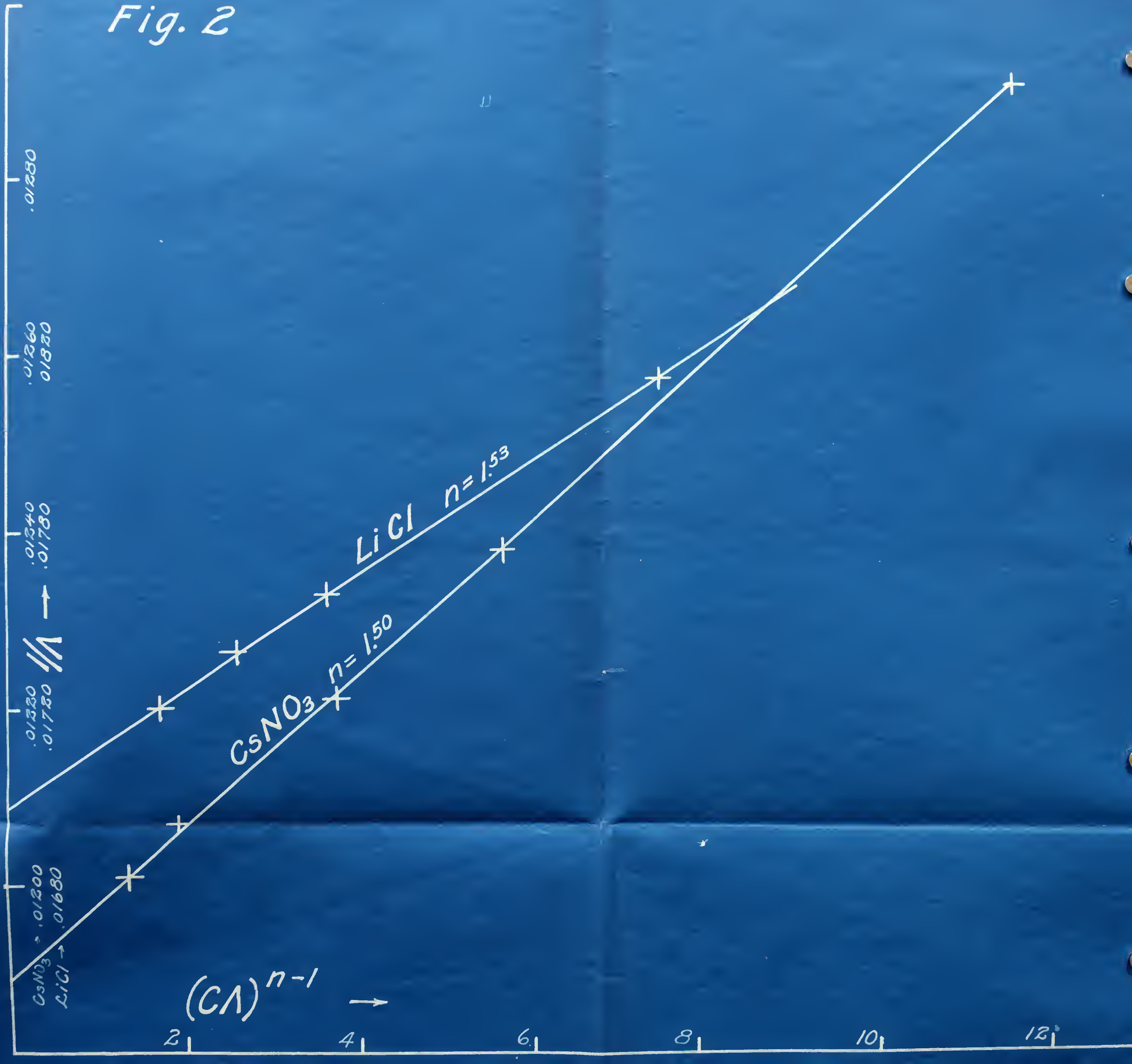


Fig. 2


Li Cl n = 1.53
CsNO3 n = 1.50
.01280
.01260
.01820
.01240
.01780
$1/\Lambda$ →
.01220
.01720
CsNO3 → .01200
LiCl → .01680
$(C\Lambda)^{n-1}$ →
2
4
6
8
10
12

infinity value of equivalent conductance must always remain uncertain to from .5 to 1 per cent as long as they are obtained by extrapolation from solutions prepared in contact with the atmosphere.

The infinity value for LiCl was obtained in the same manner as that for caesium nitrate. The value of n in the exponent of the function $(C\Lambda)^{n-1}$ was found to be 1.53. The solutions employed in this extrapolation were Nos. 9, 10, 11 and 12 of Table 4. The points for these solutions are shown graphically in figure 2. The infinity value(60.31) is estimated to be known with a precision of about seven units in the second decimal place.

To potassium chloride Noyes and Coolidge (15') assign the value of 81.4 for the equivalent conductance at infinite dilution at 0°. J. Johnston by an extrapolation based upon the same experimental data (i.e. those of Kahlenburg and of Whethan) finds the values 81.9 and 81.5. We have repeated this extrapolation but have included the results of Kohlrausch (15'') for 0.010, 0.02 and 0.1 normal potassium chloride solutions and have obtained the value 82.0. This gives more normal values for the degree of ionization of this salt in dilute solutions. Owing, however, to the inaccuracy of the data for the dilute solutions and the long extrapolation which must be made, this value must be regarded as uncertain by at least 8 units in the first decimal place.

(15') l.c. Note No. 15

(15'') Kohlrausch und Holborn "Leitvermogen der Elektrolyt" pg. 204

8-The Calculation of the Degree of Ionization.

In dilute solutions it is customary to calculate the degree of ionization from the equation Λ/Λ_∞. This relation is based upon the assumption that the nature of the medium through which the ions are moving is practically the same as that of the pure solvent. A glance at column 4 of table 6 shows, however, that even in solutions no more concentrated than 0.1 normal the viscosity of the medium may be as much as two per cent different from that of the pure solvent. It is clear, therefore, that any attempt to calculate the degree of ionization for more concentrated solutions than this must take into account the change in the character of the medium through which the ions are moving.

¶It has been proposed by several observers[15)] that the degree of ionization be calculated from the equation $\frac{\Lambda\eta}{\Lambda_\infty\eta_0}$. This relation, values for which are given in column 9 of Tables 6, 7 and 8 for the three salts investigated, can be derived from Stoke s' Theorem on the assumption that the ion is a small sphere, and that it is much larger than the particles which make up the medium through which it is moving. Since, however, neither of these assumptions is true for ions in aqueous solutions some modification of the form should be made. The work of Greene[16)] on solutions of lithium chloride to which sucrose was added, has demonstrated the fact that the mobility of the lithium and chlorine ions is not proportioned to the first power of the fluidity of the medium, but to approximately the 0.7 power. Therefore, in calculating the degree of ionization, we shall make use of the relation

$$\gamma = \left(\frac{\Lambda\eta}{\Lambda_\infty\eta_0}\right)^m \qquad (4)$$

where m is a number less than one, but greater than 0.7. In order to find m

---

15-e.g. Bonsfield and Lowry. Phil. Trans. (A) 204, 253 1905

16-J. Chemical Soc. 93, 2023 and 2049, (1908)

for a given salt we shall make the assumption that changes of viscosity produced by the presence of the salt itself affect the mobilities of its ions according to the same law as do changes of viscosity produced by moderate changes in temperature, i.e. in both cases the mobilities are proportional to the m^th^ power and that m has the same value. In order to calculate the value of m for a given salt we need only to know the value of its equivalent conductance at infinite dilution for two temperatures, together with the values for the fluidity [f of water for the same two temperatures. This gives us the two equations

$\Lambda_{o_1} = K f_1^{\,m}$ and $\Lambda_{o_2} = K f_2^{\,m}$ from which m can be obtained.

J. Johnston[17] has shown that an equation of this form expresses accurately the relation between Λ_o and f for wide temperature ranges. In table 9 are shown the values of the equivalent conductances of caesium nitrate, potassium chloride and lithium chloride at 0° and 18° respectively, together with the viscosity of water. The last column of the table gives the values of m for these three salts computed from these data as described above. The values for the fluidity of water are those of Thorpe and Rodger as corrected by Greene[18]. The equivalent conductances at 18° are those of Kohlrausch corrected to the basis of the 1910 atomic weight table.¶ In column 10 of tables 6, 7 and 8 are recorded the values of the degree of ionization as calculated from the equation $\left(\frac{\Lambda\,\eta}{\Lambda\,\eta_o}\right)^m$ using the values of m given in table 9 . The probable error in γ arising from the uncertainty in the experimental data is given at the head of each column. It is evident from columns 7, 8 and 9 that the values of γ as calculated from equation 4 do not differ from those calculated from the conductivity ratio itself by more than two per cent in the case of the caesium nitrate and potassium chloride solutions. With the lithium chloride the difference is larger, as is necessarily the case whenever the solutions have a relative viscosity greater than one.

---

[17] -J. Am. Chem. Soc. 31, 1010 ,(1909)

[18] -l.c. Note No.16

Table 9

	0°		18°		
	Λ_∞	f	Λ_∞	f	$m.$
$CsNO_3$	84.0		129.9		0.826
KCl	82.0		130.2		0.880
LiCl	60.3		98.93		0.940
H_2O		0.01792		0.01058	

9-Caesium Nitrate and The Mass Action Law.

In 1902 W. Biltz published[19] a set of freezing point data for aqueous soltions of caesium nitrate. From these data he calculated, in the usual manner, a set of values for the degrees of ionization of the salt in the different solutions studied. On substituting these values in the Ostwald Dilution Law he found that the values of K thus obtained did not exibit the usual regular variation with the concentration shown by other electrolytes, but showed irregular variations about a mean value of 0.34, throughout the concentration range 0 to 0.43 normal. The values of K which he thus obtained are shown in column VIII of the table given below. (Table 10 .)

From these results Herr Biltz drew the following conclusions: "Das Caesiumnitrat folgt dem Massenwirkungsgesetze exakt. - - - Caesiumnitrat ist demnach der erste starke Electrolyt, dessen Dissociationsverhältnisse genau bekannt sind. Dadurch ist zugleich die Annahme widerlegt dass die Abweichungen von dem Massenwirkungsgesetze durch die Anwesenheit von Ionen in grösserer Zahl prinzipiell bedingt sind. Der Grad der Dissociation hat, wie man auch schon aus dem zuerst gegebenen Versuchsmaterial ersehen konnte, keinen erkennbaren Einfluss a auf die Grösse der Abweichungen, vorausgesetzt, das man γ aus Gefreierpunktserniedrigungen berechnet."

The results obtained in this investigation do not confirm the data given by Biltz and the conclusions to which they lead regarding the behavior of this electrolyte with reference to the Law of Mass Action are also somewhat different from those arrived at by this investigator. In view of the frequent citations[20] to the"exceptional"behavior of this

---

[19] Z. physik. Chem., 40, 218, (1902)

[20] e.g., Abegg's "Handbuch der Anorganischen Chemie." Band II (2)S.450; Weinstein's "Thermodynamik und Kinetik der Körper" Band II(2) S. 716; Morgan's"The Elements of Physical Chemistry" pg. 319.

No.	I	II	III	IV	V	VI	VII	VIII	IX
	η'	V_B	V_W	Δt_B	Δt_W	Y_B	Y_W	$100\ K_B$	$100\ K_W$
		Biltz	W. & M.	Biltz	W. & M.				
1	0.00766	130.7	130.5	0.028	0.028	98	96 + 14	33	18 + 70
2	.0194	51.6	51.6	.070	.068	95	88 + 6	35	13 + 8
3	.0465	21.6	21.6	.164	.157	90.7	81 + 2	(41)	16.6 + 3
4	.0988	10.2	10.17	.331	.322	81.0	75 + 1	34	22.1 + 1.6
5	.1421	7.09	7.09	.460	.453	75.0	71.5 + 0.8	32	25.3 + 1.2
6	.2100	4.81	4.81	.662	.650	70.4	66.4 + 0.5	35	27.2 + 0.8
7	.2987	3.39	3.40	.907	.894	64.1	60.9 + 0.4	34	27.6 + 0.6
8	.3861	2.62	2.64	1.125	1.124	57.5	56.4 + 0.3	.30	27.6 + 0.4
9	.4339	2.33	2.356	1.267	1.248	57.8	54.6 + 0.2	.34	27.9 + 0.4
10	.5000	----	2.05	----	1.419	----	52.6 + 0.2	---	28.6 + 0.4

salt, which one sees in the literature, it seems advisable to present the bearing of the present results upon this question in considerable detail in the hope that it may serve to place the whole question in a clearer light.

Column I of Table 10 gives the compositions of the solutions investigated by Biltz, column IV contains the corresponding freezing point lowerings found by him and column V shows the freezing point lowerings given by the empirical equation (1) pg. 13. A comparison of the two sets of data shows that from a concentration of 0.05 molal up all of Biltz's values differ from mine by from 0.01 to 0.02° except in the case of solution number 8, for which the values are identical.

If an electrolyte be regarded as a normal solute and the solution be sufficiently dilute its degree of ionization is given by the equation:

$$\gamma = \frac{\Delta t}{K_F n'} - 1 \qquad (5)$$

where k_F is the molal freezing point lowering. The theoretical value for k_F as computed from the relation $\frac{RT_0}{L_0}$ is 1.86° for water. This value is moreover confirmed by the recent careful freezing point measurments of Bedford[21] who found for cane sugar solutions the value 1.86° and for potassium chloride solutions the value 3.72° = 2 x 1.86° at high dilutions.

At the time of Biltz' investigation, 1.85° was the generally accepted value for k_F and he employed this value in calculating the degree of ionization of the caesium nitrate in the solutions investigated by him. His results for 100 γ are shown in column VI of table 10. If however the value 1.86° is employed and the values for Δt given in column V are used, the values for 100 γ shown in column VII are obtained. The deviation which would be caused by the probable error in the corresponding value of Δt is also indicated after each value in this column[22].

21-Proc. Roy. Soc. Lon. (A) 3, 434(1910)

22-These deviations are calculated from the relation: $d\gamma = \frac{d(\Delta t)}{1.86 n'}$

It is evident that below 0.05 normal the values are too uncertain to be relied upon. Those above 0.3 normal will also be somewhat in error from the fact that equation (5) is only applicable to dilute solutions. With an accuracy of 0.002° in Δt the values of γ for solutions of greater concentrations than 0.3 normal should be computed from an equation which does not involve the laws of dilute solutions. This will be done in section 10 below.

In order to test the Mass Action Law for caesium nitrate solutions Biltz substituted the values for γ from column VI and the values for V from column II in the Ostwald Dilution Law-

$$\frac{\gamma^2}{(1-\gamma)V} = K \qquad (6)$$

and obtained the values for $100K$ given in column VIII. These values evidently vary irregularly, and rejecting Nos. 3 and 8 Biltz adopted 0.34 as the mean value for K

If the values for γ given in column VII and the values[23] for V of column III be employed, the values for $100K$ shown in column IX are obtained. After each value in this column is given the deviation[24] which would be produced by the probable error in the corresponding value of Δt.

These values are shown graphically in curve III of fig. 3. Values of n' are plotted as ordinates and the values of $100K$ as abscissae. On either side of each point is drawn a line equivalent in length to the probable error in the location of the point. An inspection of this curve shows that K increases fairly rapidly up to a concentration of about 0.2 normal. From thence up to 0.5 normal it is constant within the limits of experimental error.

Now the Ostwald Dilution Law has no theoretical basis except for

---

[23] These are computed from my density data at 0°. They are substantially identical with those of Biltz.

[24] These deviations are computed from the equation:

$$dK = \left[K + \frac{\Delta t}{0.93} - \frac{2}{V}\right]\frac{d(\Delta t)}{3.72n' - \Delta t} \qquad \text{if } \Delta t \not> 3^\circ$$

very dilute solutions and it is exactly in this region that it is not obeyed by caesium nitrate. If we wish to study this equilibrium in concentrations above 0.1 normal it will be better to employ a more general law for chemical equilibrium, one which does contain the assumption that the solution is dilute.

10- Caesium Nitrate and the General Law for Chemical Equilibrium.

The general law for chemical equilibrium in an "ideal" or "perfect" solution is expressed by the equation:[25)]

$$\frac{N_A^a\, N_B^b}{N_M^m\, N_N^n} = K_N \qquad (7)$$

This differs from the Ostwald Dilution Law only in the substitution of mol fractions in place of volume concentrations. For the dissociation of a binary electrolyte it assumes the form-

$$\frac{N_i^2}{N_U} = K_N \qquad (8)$$

where Ni is the mol fraction of each ion and N_U the mol fraction of the unionized molecules.

If the solvent is water and the degree of ionization of the salt is γ_N and its concentration is n' mols per 1000 grams of water, we have:

$$N_i = \frac{\gamma_N n'}{\frac{55.53}{A} + (1+\gamma_N)n'} \quad \text{and} \quad N_U = \frac{(1-\gamma_N)n'}{\frac{55.53}{A} + (1+\gamma_N)n'} \qquad (9)$$

and equation (7) becomes

$$\frac{(\gamma_N n')^2}{\left[\frac{55.53}{A} + (1+\gamma_N)n'\right]\left[1-\gamma_N\right]n'} = K_N \qquad (10)$$

in which A is the association factor of water, i.e., 18 A is the average molecular weight of the water at the temperature in question.

Calculation of γ_N. In order to calculate γ_N from the freezing point data, use will be made of the relation[26)] connecting the freezing

---

25-For a derivation of this equation and a more complete discussion of the "ideal" solution see Washburn, Z. physik. Chem., 74, 558 (1910): J. Am. Chem. Soc., 32, 668 (1910); J. Chim. Phys. 8, 564 (1910).

26-For the general statement and derivation of this relation see Washburn, loc. cit.

point lowering and mol fraction in the case of an "ideal" solution. If water is the solvent and the solution is only moderately concentrated it has been shown by Washburn[27] that the following equation[28] is a sufficiently exact numerical statement of this relation

$$N' = 0.00969\,\Delta t(1 - 0.0043\,\Delta t) \qquad (11)$$

If we replace N', the mol fraction of the solute, by $\frac{in'}{\frac{1000}{18} + in'}$, this equation takes the form[29]

$$in' = \frac{\Delta t}{1.858}(1 + 0.0055\,\Delta t) \qquad (12)$$

If the electrolyte is not hydrated, the Van't Hoff i or the "mol number" is equal to $(1 + \gamma)$ and we may therefore employ this equation in order to obtain the degree of ionization of an unhydrated electrolyte. Now caesium nitrate is probably the least hydrated of all electrolytes and we shall therefore proceed upon the assumption that its hydration can be neglected[30] in applying equation (11). This procedure also necessarily assumes that γ does not change appreciably with temperature over the range involved. (See page)

The values for the percent of ionization, 100γ, computed upon this basis are shown in column IV of table 11, together with the probable errors arising from the uncertainties in the Δt values. These values, as

---

27-Washburn, Technology Quarterly, 21, 373 (1908) and Jahrb. Rad.u. Elektronik, 5, 493.

28-This equation has been applied (loc.cit. Tech. Quart.) to the freezing point data for nonelectrolytes in aqueous solution and has been shown to hold for non hydrated solutes over a considerably greater range of concentrations than is involved in the present investigation.

29-Noyes and Falk (J. Am. Chem. Soc., 32, 1013 (1910) have recently applied this equation to all the existing freezing point data for electrolytes and have tabulated values for the "mol number" i, for 42 electrolytes for different concentrations up to 0.5 molal.

30-At least one mol of water would have to be in combination with each molecular weight of the salt in order to produce an error of one per cent in the value of $(1+\gamma_N)$.

I	II	III	IV			V			VI		
n'	Δt + 0.002°	100 N'	100γ			100 K A = 2			100 K A = 3		
0.0250	0.084	0.082	82	±	4	3.4	±	0.8	5.1	±	1.2
.0500	.167	.162	80	±	2	5.6	±	0.6	8.4	±	0.9
.0750	.247	.239	77	±	1	7.0	±	0.4	10.5	±	0.6
.1000	.325	.315	75	±	1	8.4	±	0.4	12.5	±	0.6
.1500	.477	.461	71.3	±	0.7	9.5	±	0.2	14.3	±	0.3
.2000	.622	.601	68.0	±	0.5	10.2	±	0.18	15.2	±	0.27
.2500	.762	.736	64.8	±	0.4	10.49	±	0.14	15.60	±	0.21
.3000	.897	.866	61.7	±	0.3	10.57	±	0.10	15.71	±	0.15
.3500	1.030	.993	59.1	±	0.3	10.63	±	0.10	15.80	±	0.15
.4000	1.160	1.118	57.0	±	0.3	10.67	±	0.08	15.81	±	0.12
.4500	1.290	1.243	55.3	±	0.2	10.84	±	0.06	16.08	±	0.09
.5000	(1.419 ± 0.005°)	1.366	(53.6	±	0.5)	11.1	±	0.26	16.40	±	0.39

Table 11 A.

m'	.025	.050	.075	.10	.15	.20	.25
1000K	8.184	11.91	14.02	15.58	18.49	20.34	22.27
n'	.30	.35	.40	.45	.50		
1000K	24.26	25.05	26.21	27.16	27.85		

computed from equation (1), are shown in column II. Column I gives the number of formula weights, n', of caesium nitrate per 1000 grams of water and column III shows the total mol per cent., 100 N'.of solute as computed from equation (12).

We will now substitute these values in the general equation for chemical equilibrium, (equation 10), and calculate the equilibrium constant K_N . Before we can do this however it will be necessary to assign some value to the association factor A. This factor is, however, not a constant, but is a function of n' and is connected with it in such a way that as n' increases A decreases, so that even if we knew the value of A accurately for pure water and employed this value in our equation, we should not expect to find a constant value for K_N , but a slowly increasing value as the concentration increases. Authorities agree that water at zero degrees is composed chiefly of double and triple molecules, so that A is probably not less than 2 or greater than 3. Two series of values for 100 K_N have therefore been computed, one upon the basis that A=2, column V, and the other upon the basis that A = 3, column VI.[31]. These values are shown graphically in curves 1 and 2 respectively in fig.3, values of n' being plotted as ordinates and values of 100K as abscissae.

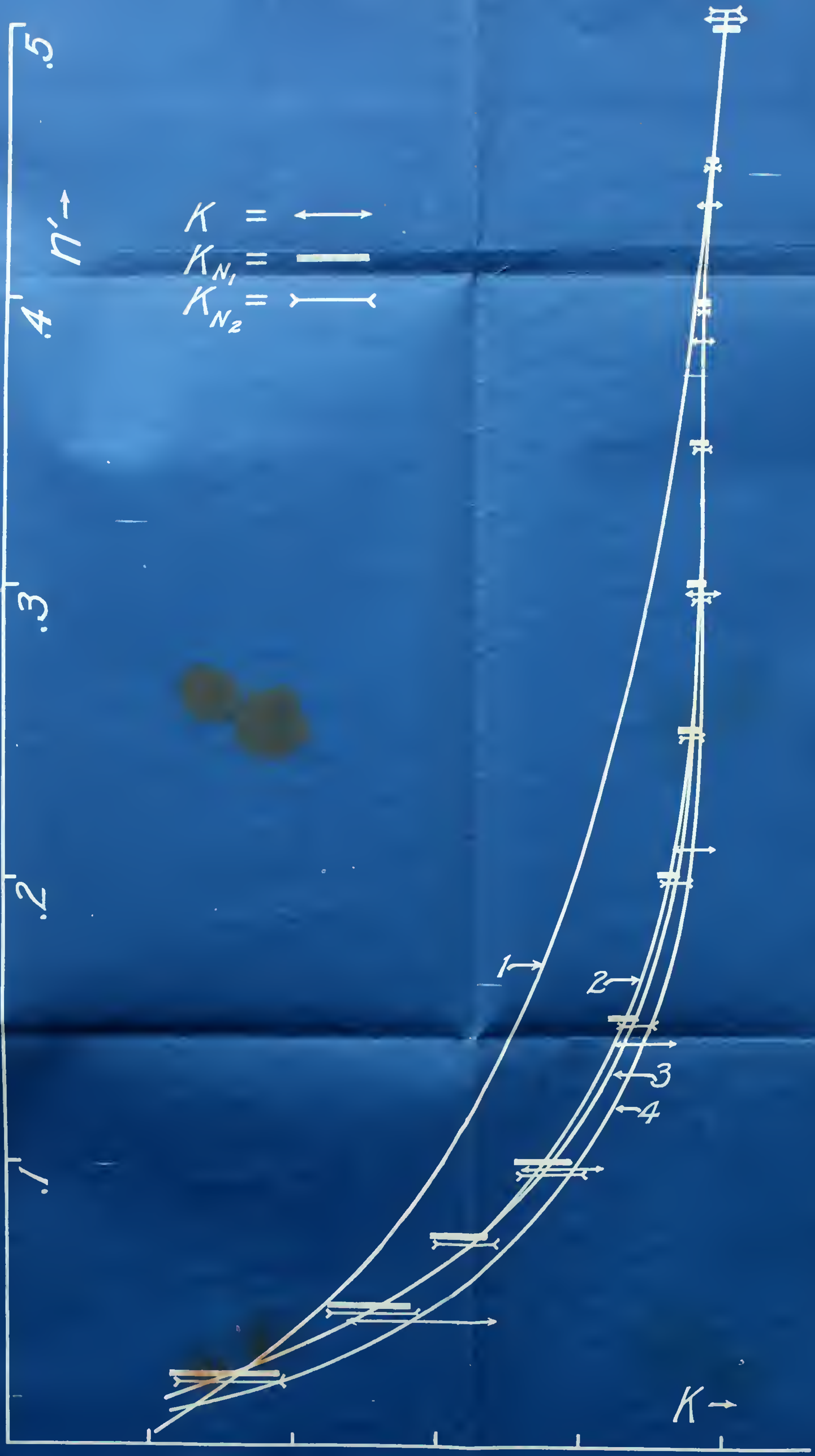
An inspection of these curves shows that between 0.2 and 0.5 normal 100 K increases slowly (from 10.2 to 11.1 for A = 2 and from 15.2 to 16.4 for A = 3) as was to be expected. The direction of the curve in the more dilute solutions would indicate that at high dilutions K_N would have a very different value.

---

[31] —The probable errors given for these values of K are computed from the relation:-

$$dK_N = \left[K_N + 0.0192\,A\,\Delta t - 0.036\,A\,n'\right]\frac{0.54\,d(\Delta t)}{2n' - 0.54\,\Delta t}$$

Fig. 5.


K =
K_{N_1} =
K_{N_2} =
n′→
.5
.4
.3
.2
.1
1→
2→
3
4
K→

In table 11A are shown values of K computed from formula 10, except that instead of γ_N values of the expression for the degree of dissociation $\gamma = \left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^m$ have been substituted. Column 9 of table 6 gives values for this function at round concentrations. This gives a test of the applicability of the Mass Law to the dissociation of caesium nitrate, when the degree of dissociation is calculated from the conductivity ratio, corrected for the change of viscosity with the concentration. The relation of the values of K thus computed, to the concentration are shown graphically in curve 1 of figure 3, and it is seen that K is not even approximately constant in the range of concentration studied.

11-Discussion of Results

If a solute is "normal", that is to say its "activity"[32] is proportional to its mol fraction, the laws of the "ideal" solution are obeyed.[33] Equation 11, page 26, gives the relation between the freezing point lowering and the mol fraction for a "normal" solute in aqueous solution. This has been found to express the results of experimental determinations for solutions of several non-electrolytes for concentration ranges considerably exceeding those of the present investigation. Curve 2 of figure 4 is a graphical representation of this relation, in which mol per cents (= 100 x mol fraction) are plotted as ordinates and freezing point lowerings as abscissae.

In column eleven (11) of tables 6, 7 and 8 are given values of the mol per cent calculated from the equation:-

$$100N' = \frac{(1+\gamma)n'}{55.53+(1+\gamma)n'} \times 100$$

(See page 25) for the three salts investigated, and in column 2 of the same tables are given the corresponding values of the freezing point lowering. The value of γ in this equation was computed from the conductance and viscosity data as described in the preceding section.

In order to compare the relations of the freezing point lowerings and mol per cents with those of an "ideal" solution, the values were plotted in Fig. 4 . Curve 1 represents the relations for caesium nitrate, Curve 3 for lithium chloride, and Curve 2, which is seen to be practically identical with the plot of the "ideal" solution equation, represents the values for potassium chloride. Column 3 of tables 6, 7 and 8 contains the freezing point depression that an electrolyte would produce if both its ionized and unionized portions were normal solutes.

---

[32]-For a discussion of this term see G. N. Lewis, Proc. Am. Acad. 43, 259; Z. physik.Chem.61,129 1907

[33]-Washburn, l. c. Note No.

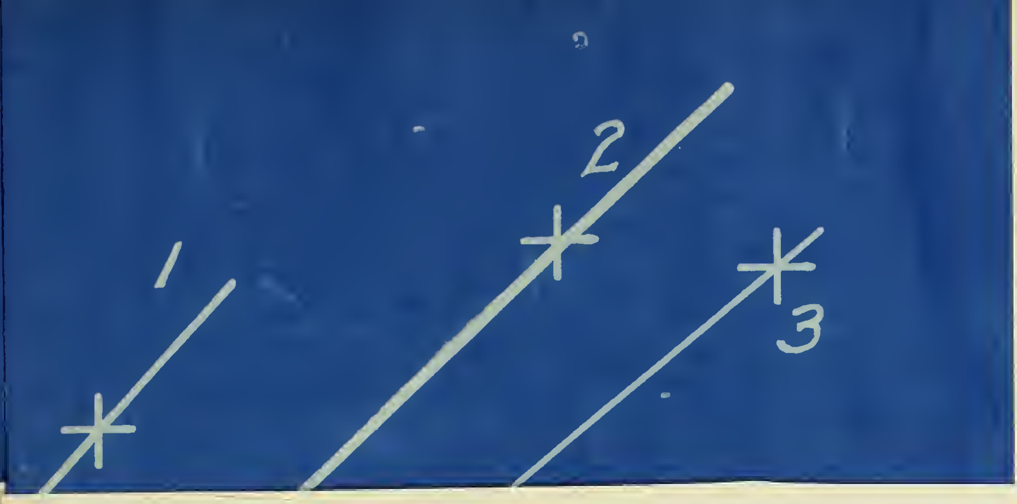
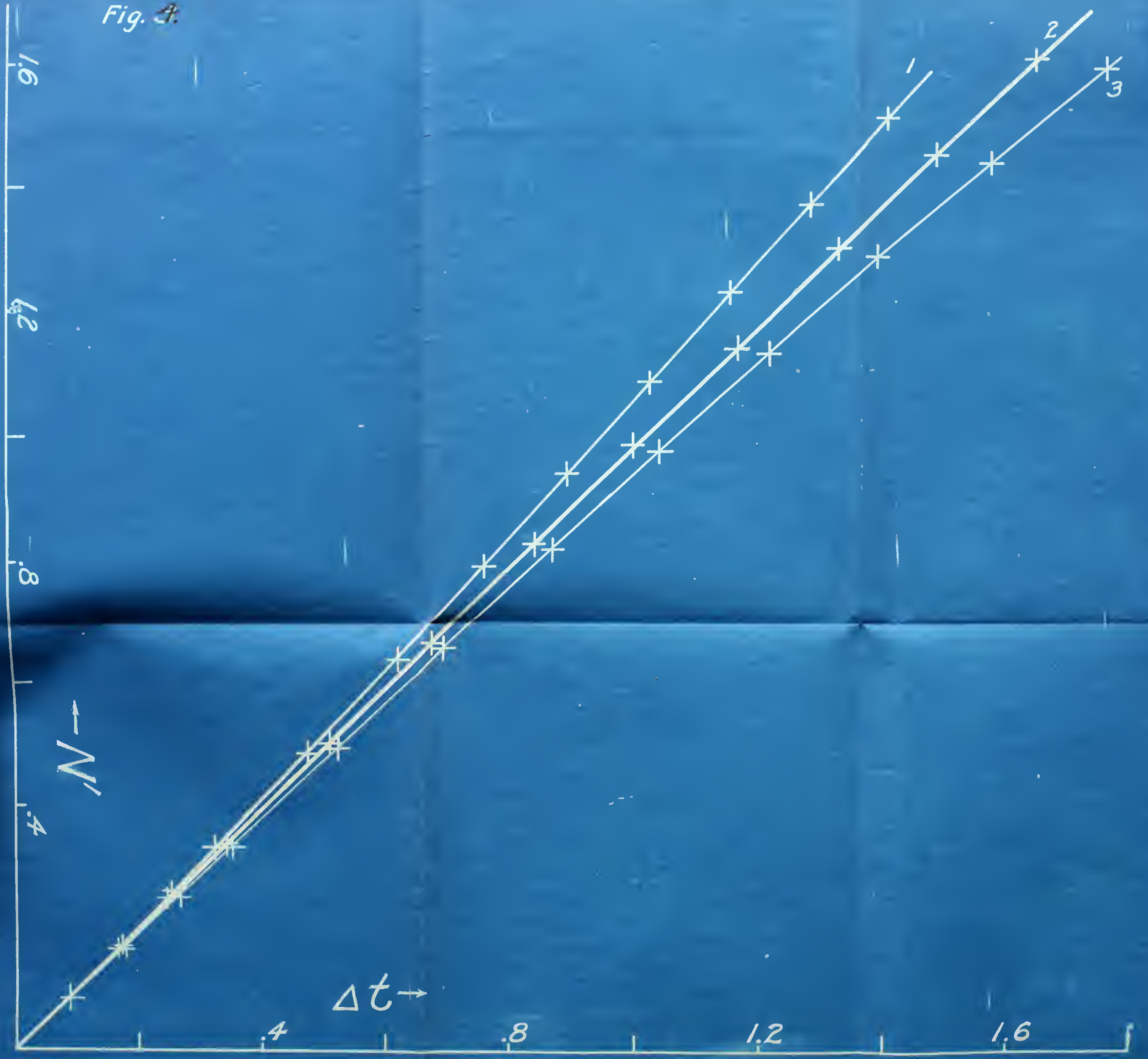


Fig. 4.



If a normal solute were hydrated, i.e. combined with a portion of the solute, its freezing point-mol fraction curve would fall below that of the "ideal" solution, as is seen to be the case with the lithium chloride curve. In the case of the caesium nitrate, however, the curve is seen to lie above that of the "ideal" solution, an abnormality for which no explanation is attempted, except that it probably is due to the electrical charges on the ions.

The fact that the potassium chloride curve is almost identical with that of the "ideal" solution can only be ascribed to coincidence. It probably represents a compensation of the deviations produced by the abnormality just referred to and that produced by hydration. It is not possible that solutions of potassium chloride are "ideal" solutions, as in that case both its ionized and undissociated portions would have to be "normal" solutes, and from the thermodynamic basis of the law of "ideal" solution, its dissociation would have to follow the mass law. As is well known, this is not the case. Further, Washburn[34)] has shown from transference measurements that the potassium ion is hydrated.

For a solution of a non-electrolyte deviations of its mol per cent-freezing point curve below that of the"ideal"solution can be used to calculate, roughly at least, the extent of the combination of the solvent with the solute, in other words, the plot of the "ideal" solution represents zero hydration for a non-electrolyte. That it does not represent zero hydration for electrolytes is evident from the case of potassium chloride just referred to, and from the fact that we would have to assume negative hydration for caesium nitrate. It is clear then, that if we are to form a quantitative estimate of the hydration of these substances, a line representing no hydration for binary strong electrolytes must be found.

34-Tech. Quart. 21, page 312, (1908); Z. physik. Chem. 66, 513,(1909)

There is evidence that caesium nitrate is unhydrated in solution, and that curve 1, fulfills the above conditions. In the alkali metal series the mobilities of the ions have been shown to follow the inverse order of their atomic weights, and caesium has the highest atomic weight of this series. The caesium ion is, therefore, probably the smallest, or least hydrated. Transference measurements in the presence of a non-electrolyte 35) lead to the same conclusions as to the relative hydration of the ions of this series. For similar reasons the nitrate ion is believed to be little, if at all hydrated. The wide divergence in a direction opposed to that produced by hydration, of the caesium nitrate mol per cent-freezing point curve from that of the "ideal" solution is also a strong indication that the solvent is but slightly combined with the solute.

If we assume that Curve I represents the mol per cent-freezing point relation for an unhydrated binary strong electrolyte, deviations from this curve can be used to determine the hydration of these substances. This will require the further assumption that the abnormality which causes the deviation of the caesium nitrate curve from that of the "ideal" solution affects the three salts studied to the same extent. This is quite probably the case, as the salts are of the same type and ionized, approximately, to the same extent.

The hydration can be determined quantitatively by the equation

$$N'' = \frac{n'(1+\gamma)}{55.53 + n'(1+\gamma) - n'x} \qquad (13)$$

where x is the number of molecules of water combined with a mol of solute and N″ is the mol fraction of the solute in a caesium nitrate solution which would have the same freezing point lowering as that produced by the addition of n′ mols of the hydrated salt. Values of N″ can be found graphically from figure 4.

---

35) l.c. Note No. 34

Solving for xn we have

$$xn' = 55.53 + n'(1+\gamma) - \frac{n'(1+\gamma)}{N''}$$

Values of xn' and x are given in table 12 in column 2 and 3 and the corresponding concentrations n' in column 1.

Table 12.

	KCl		LiCl	
n'	$n'x$	x	$n'x$	x
.5	5.2	10.3	9.0	18.
.45	5.1	11.3	8.4	18.6
.4	4.9	12.3	7.7	19.0
.35	4.7	13.4	7.2	20.6

It is seen that the number of mols of water combined with a mol of solute, x, decreases with the increasing concentration of water as would be expected from the effect of mass action.

Washburn l.c) in his "Transference Measurements in the Presence of a Nonelectrolyte" measured the difference of the amounts of water combined with the different ions. Ascribing whole numbers for the hydration of the chlorine ion he obtained a table of which the following is an abbreviation.

Cl	H^+	K^+	Na^+	Li^+
2	0.65	3.3	5.2	9.3
--	----	----	---	---
4	1.02	5.4	8.4	13.9
---	---	---	---	----
6	1.4	7.4	11.6	18.5

The value of 4 for the hydration of the chlorine ion is a probable one as it avoids giving a fraction as the hydration of the hydrogen ion. Also, it is seen that with this value for the hydration of the chlorine ion the corresponding values for the hydration of the potassium chloride and lithium chloride are 9.4 and 17.9 which are of the same order of magnitude as the values given in table 12.

Biographical

The writer received his early education in the schools of Salt Lake City, Utah. In the fall of 1899 he entered the preparatory school of the University of Utah, and in 1907 he graduated from that institution with the degree of Bachelor of Science in Chemical Engineering. During 1907 and until the fall of 1908, he did chemical and engineering work in Nevada. In the fall of 1908 he entered the University of Illinois as scholar in Chemistry and at the end of that college year received the degree of Master of Science in Chemistry. During the college years 1909-10 and 1910-11 he held a fellowship in the University of Illinois.

He is a member of Sigma Xi, Phi Lambda Upsilon and Gamma Alpha Fraternities.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 086858120